The Acetylation of Starch by Reactive Extrusion

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glucosidase attack, thus indicating that these fractions were involved in the waxy corn starch crystallyne areas. Both the debranched α-glucans from both non-separated (N) and small (S) starch granules presented three distint groups of unit chains, instead of the two previously reported. Amylopectins from both starch granules studied appeared to have identical structures.

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The Acetylation of Starch by Reactive Extrusion

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Potato starch has been acetylated in a counter rotating twin screw extruder using vinylacetate and sodium hydroxide. The desired starch acetylation reaction is accompanied by an undesired parallel base catalysed hydrolysis reaction of vinylacetate and a consecutive hydrolysis reaction of the acetylated starch. Also deacetylation may occur.
During the extrusion process sodium hydroxide, vinylacetate, granular potato starch and water were supplied to the extruder. Conversions up to 100 % could be achieved. The degree of substitution could be varied from 0.05 to 0.2. Selectivities from vinylacetate towards starch of up to 80 % could be achieved. From reaction kinetics and experiments it could be concluded that the deacetylation reaction could be neglected. The degree of gelatinisation appeared to be a major key parameter. Increasing the gelatinisation in an early stage of the extrusion process, at high starch concentrations and temperatures, increases the selectivity and degree of substitution. The gelatinisation degree can be increased by applying high shear and temperatures to the starch granule and by using screws with modified geometries.

1 Introduction

The acetylation of starch is a chemical modification, known for more than a century *Jarowenko* [1]. In the modified starch, part of the hydroxyl groups of the glucose monomers have been converted into o-(-ethanoate) groups. Highly acetylated starches with a degree of substitution (DS) of 2 to 3 were of research interest from 1950 through 1980 for their solubility in acetone and chloroform and for their thermoplasticity *Wolff* et al. [2]. Because they could not compete with similar cellulose derivatives in terms of costs and strength, they have not been developed commercially. Low acetylated starches with a DS of 0.01 to 0.2 are still of commercial interest. Their usage is based on properties with respect to film forming, binding, adhesivity, thickening, stabilising and texturing.

Acetylated starch can be produced in a direct way using acetic acid. However this equilibrium-controlled reaction is not recommended because the reactants formed should be removed to obtain high conversions *Roberts* [3]. Other possible reactions use acetic anhydride, acetylchloride or vinylacetate. All these esterifications are kinetically rate controlled.

Production of acetylated starch using vinylacetate is commercially performed in an aqueous medium in the presence of alkali. The suspension is buffered with sodium carbonate to a pH of 9 to 10. After 1 h of reaction at 311 K, the reaction medium is acidified with dilute sulphuric acid to a pH of 6 to 7. The starch is recovered by filtration, washing and drying.

Joosten et al. [4] presented a design of a tubular reactor for a commercial acetylation process. All processes mentioned above have in common that a slurry of starch in water is used. The hydroxide concentration and the temperature have to be kept low to prevent the gelatinisation of starch, that would lead to serious mixing problems. These low temperatures and hydroxide concentrations result in low conversion rates and selectivities. Reactions in aqueous solutions can be conducted at higher temperatures, but the starch concentration must be kept low, again to prevent mixing problems that can arise due to the increase of viscosity.

Twin screw extrusion is an alternative to this problem, mainly because extruders have proven to be very suitable for the handling and mixing of highly viscous polymer melts or solutions and performing reactions in these media *Ganzeveld* et al. [11], *Berghaus* et al. [21], *Bartilla* et al. [22], *Bouilloux* et al. [23].

The objective in the present study is the description of the influence of different reaction parameters like the temperature, the water concentration, the vinylacetate concentration, the starch concentration and the NaOH concentration on the acetylation of starch during the extrusion in a counter rotating twin screw extruder.

2 Theory

2.1 Starch

Starch consists primarily of two polymers, the linear amylose and highly branched amylopectin. These two polymers are present as birefringent, semi crystalline granules in all higher plants. The crystallinity is associated with the amylopectin component [5, 6]. Short chains of amylopectin pack as double helices into crystalline lamellae *Yamaguchi* et al. [7], these crystalline lamellae alternate with amorphous lamellae where amylopectin branch points are located. Between these structures, amorphous rings exist, where it is believed that most of the amylose is deposited.

When starch is processed in extruders the granular structure undergoes, due to heat and shear, an order-disorder transition termed gelatinisation. During gelatinisation the granules swell as they absorb water. This swelling occurs mainly in the amorphous amylose layers *Jenkings* et al. [8] and amylose is able to leach out of the granule. The amylopectin double helices in this region dissociate, and the granule rapidly loses all crystallinity. This process can be accelerated by shear.

2.2 Extruders

The counter rotating twin screw extruder, used in this work, is closely intermeshing and consists of series of C-shaped chambers in which material is transported towards the die. Interactions between the chambers occur through

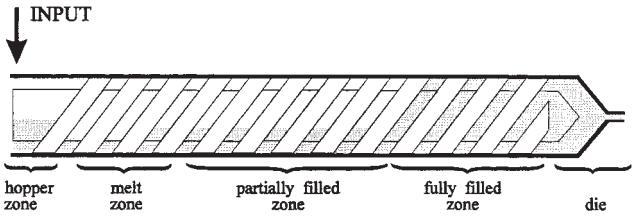


Fig. 1. Schematic representation of the extruder.

various leakage gaps. According to *Janssen* [9] four gaps exists. The *flight gap* (Q_f), this is a clearance between the barrel and the flight of the screws. The *tetrahedron gap* (Q_t), this gap connects the consecutive chambers on the opposite, screws and is situated between the flight walls. The *calender gap* (Q_c). This gap is formed by the clearance between the flight of one screw and the bottom of the channel of the other screw and resembles a calander. The *side gap* (Q_s), this is a gap between the flanks of the flights of the two screws. Three zones can be distinguished from hopper to die (Fig. 1).

The solids transport zone; the feed material enters the extruder as granules or as powder in this zone. *The partially filled zone;* due to the increased heat and the addition of water starch start to gelatinise. In this zone no pressure is being build up. *The pump zone/fully filled zone*; the pressure on the gel is increased due to completely filled C-shaped chambers. The major part of the mixing, kneading and heat transfer takes place in this zone. Therefore, this zone is of extreme importance for the efficient functioning of the twin screw extruder and is characterised by the number of C-shaped chambers that are fully filled with a starch gel. When the pressure drop over this zone is known the amount of fully filled chambers can be calculated:

$$\nu_f = P_{die}/\Delta P_c = \eta Q_r/K \Delta P_c \quad [1]$$

In which P_{die} is the die pressure, ΔP_c, is the pressure difference between two consecutive chambers, Q_r is the real throughput, η the viscosity of the material and K is the reciprocal die resistance. The ideal theoretical throughput Q_{th} of the pump zone is given by the number of C-shaped chambers becoming free per unit time, multiplied by the volume of one chamber. For a twin screw extruder with m thread starts per screw:

$$Q_{th} = 2\ m\ N\ V_c \quad [2]$$

The real throughput (Q_r) is equal to the difference between the theoretical throughput and the leakage flows:

$$Q_r = Q_{th} - Q_{leak} = Q_{th} - Q_t - 2\ Q_f - 2\ m\ (Q_c + Q_s) \quad [3]$$

All leakage flows consists of a drag flow component, which depends on the rotational speed N, and a pressure flow component, which is a function of the local pressure difference:

$$Q_{leak} = AN + B\ \frac{\Delta P_c}{\eta_c} \quad [4]$$

The parameters A and B are functions of the screw geometry only *Janssen* [9], N is the screw speed, ΔP_c is the pressure difference between two C-shaped chambers and η_c is the viscosity of the material processed. Experimentally, it has been verified that the passage of material through high

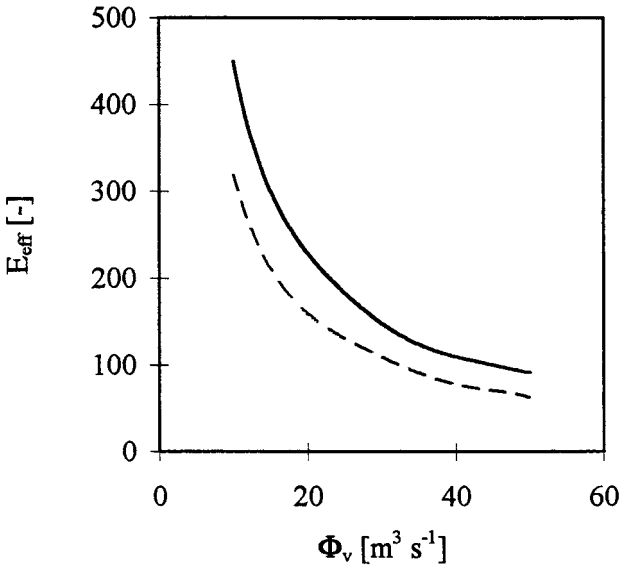


Fig. 2. Mixing efficiency versus the throughput for different screw geometries. All other parameters were kept constant. N 15 RPM, v_f = 4, — : Wide screws, (L/D = 6), – –: Narrow screws (L/D =8).

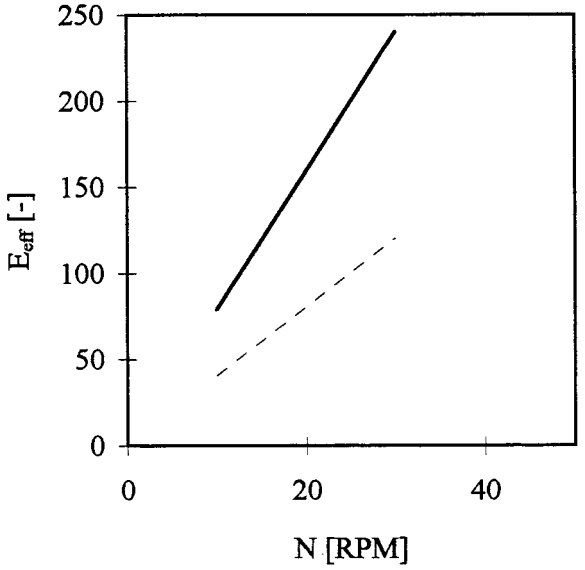


Fig. 3. Mixing efficiency versus the screw speed for different screw geometries. All other extruder parameters were kept constant. Q_{real} = 35 gmin^{-1}, v_f = 4, —: Wide screws (L/D = 6), – – –: Narrow screws (L/D = 8).

shear and elongation flow fields is necessary to increase the rate of gelatinisation of starch *Lawton* et al. [10]. These flow fields can be found in the leakage gaps. The number of passages through these gaps is thus an important parameter. Two mixing parameters can be defined by *Ganzeveld* et al.[11]:

1. The mixing efficiency, being the average number of passages of a starch granule through a high shear region.
2. The mixing deficiency defined as the fraction of material that does not pass through these high shear regions.

In the case of constant viscosity the mixing efficiency becomes:

$$E = \frac{B}{2K} + \frac{v_r AN}{2Q} \qquad [5]$$

In which v_r is the total amount of C-shaped chambers, AN is the rotation dependant part of the leakage flow and B/2K is the pressure dependant part of the leakage flow, K is the reciprocal die resistance. In the Figures 2 and 3 trendlines are plotted for the two screw pairs used in our experiments.

2.3 Kinetics

In order to determine the kinetics of the reaction, the acetylation of potato starch by vinylacetate has been carried out in aqueous suspensions of starch under alkaline conditions at temperatures lying between 323 K and 373 K. Starch dissolved in water has a weak polyacid nature [12, 13]:

$$ROH + H_2O \xleftrightarrow{K_{eq}} RO^- + H_3O^+ \qquad [a]$$

K_{eq} is the dissociation constant of starch in water and is defined as:

$$K_{eq} = \frac{(c_{RO^-} c_{H_3O^+})}{(c_{ROH} c_{H_2O})} \qquad [6]$$

This dissociation constant has been determined by several authors [12, 14]. The amount of RO^- present in our reaction medium was calculated from *Lammers* et al. [13]:

$$pK_{eq} = 12.2 + 12\ 10^3/T \qquad [7]$$

When NaOH is added to a starch solution the hydroxyl groups of the starch react according to:

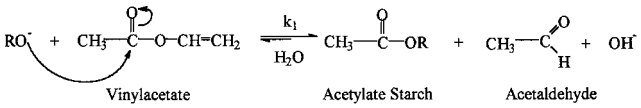
$$ROH + OH^- \xleftrightarrow{K_s} RO^- + H_2O \qquad [b]$$

K_s is the dissociation constant of dissolved starch in an alkaline medium and can be defined as:

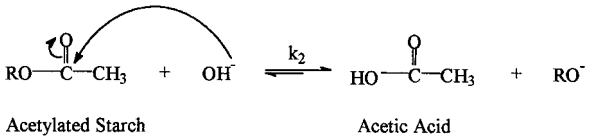
$$K_S = \frac{(c_{RO^-} c_{H_2O})}{(c_{ROH}\ c_{OH^-})} \qquad [8]$$

The dissociation constant for this reaction is equal to K_{eq} (starch dissociation in water) divided by K_a, (the dissociation constant of water). Beside these equilibria, the following chemical reactions are involved:

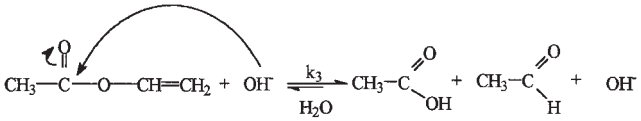
The acetylation of the hydroxyl groups of the starch molecules:



The deacetylation of starch:



Hydrolysis of vinylacetate:



The reactions proceed according to a nucleophilic substitution at the unsaturated carbon. Sodium hydroxide acts as

promoter. Both the hydrolysis reactions produce acetic acid which is neutralised by a fast reaction with a hydroxide ion. For all reactants a first order dependency is measured [15, 16, 17] resulting in the following reaction rate equations:

Starch acetylation: $R_{RAc} = k_1 c_{ViAc} c_{RO^-}$ [9]
Starch acetate hydrolyses: $R_{-RAC} = -k_2 c_{RAc} c_{OH^-}$ [10]
Vinylacetate hydrolyses: $R_{ViAc} = -k_3 c_{ViAc} c_{OH^-}$ [11]
where $k_{1,2,3} = k' c_{H_2O}$.

The reaction rate constants and concentration dependencies are measured by several authors [15, 16, 17]. The reaction rate constants as a function of temperature satisfy an *Arrhenius* equation. The activation energy (E_a) and frequency factor (k_∞) of the three reaction are tabulated in Table 1. Values of the rate constants were calculated from the *Arrhenius* equations. [RO^-] concentrations in the reaction mixture were calculated from the pK_a, of the starch, taking into account the actual water concentration in the starch solution. In this way the vinylacetate selectivity for the different reactions at different starch concentration and temperatures could be calculated.

$$\sigma_{AS} = \frac{k_1 c_{Viac} c_{RO^-} - k_2 c_{RAc} c_{OH^-}}{k_1 c_{Viac} c_{RO^-} - k_2 c_{RAc} c_{OH^-} + k_3 c_{Viac} c_{OH^-}} \quad [12]$$

Figure 4 shows a plot of the initial selectivity as a function of the temperature at several starch water ratios. Due to the higher activation energy of the acetylation reaction, the selectivity increases at higher temperatures and starch concentrations.

Tab. 1. Activation energy and frequency factor for the reaction rate constants of the participating reactions.

	$E_{A,\infty}$	k_∞
k_1 (Acetylation reaction)	93200	$1.14\ 10^{14}$
k_2 (Deacetylation reaction)	46650	92.8
k_3 (Hydrolysis of vinylacetate)	31975	1840

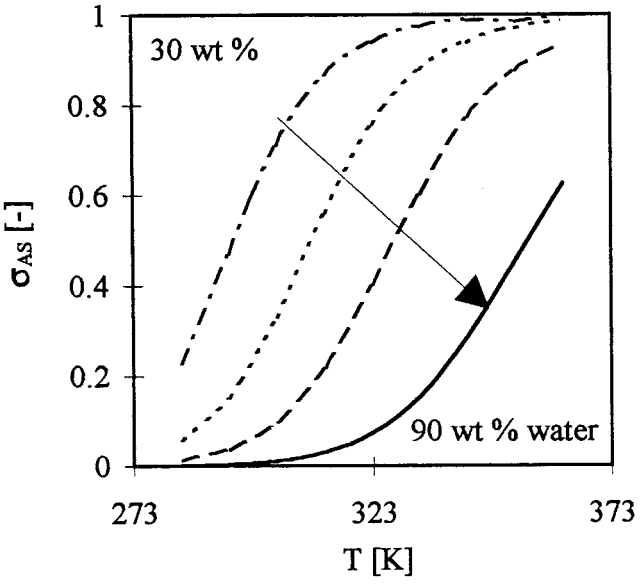


Fig. 4. Selectivity towards acetylated starch as a function of temperature and starch concentration (pH = 8.5, $c_{Viac,s}$ = 0.3 kmol kg^{-1} water). From the top line downwards: 30 wt%, 50 wt%,70 wt% and 90 wt% water.

3 Experimental

3.1 Equipment and materials

During the experiments a counter-rotating closely-intermeshing twin-screw extruder was used with a screw diameter of 50 mm. This extruder has two sets of screws, one with a length of 40 cm (L/D = 8) and leakage gaps of about 0.1 mm. The other screw has a length of 30 cm (L/D = 6) and leakage gaps of about 1 mm. In the case of the short screw three heating zones were used. For the longer screw four heating zones were used. The basic settings of the extruder are given in Table 2. The different parameters were varied one at a time while the other parameters remained those of the basic setting. The pressure profile over the extruder was measured with three pressure transducers. The output of the extruder ranged from 1.8 kg h^{-1} to 2.4 kg h^{-1}.

The potato-starch was delivered by AVEBE (Holland) (Food Grade, production year 1991). The vinylacetate and the sodium hydroxide were pro analysis grade products of Merck, Germany.

3.2 Experimental procedure

After the extruder was preheated a composition of starch, water, sodium hydroxide and vinylacetate was fed to the extruder. The starch contained about 15 wt% water. During the experiments the screw speed, the screw type, the die pressure, temperature profile and all reactant concentrations were varied. Samples were taken when a stable temperature- and pressure profile along the extruder was obtained. To stop the reaction, samples were quenched in liquid nitrogen, grinded and precipitated in a solution of 100 ml methanol and 10 ml titrisol buffer of pH = 7. The pH value was controlled using a pH-electrode (Schott Geräte). The white precipitated powder obtained was washed with methanol and dried in a vacuum oven.

3.3 Analysis

From the samples taken the degree of substitution (DS) could be determined. The DS is the number of vinylacetate molecules which have reacted to a number of hydroxy-molecules on an anhydroglucose unit. The maximum achievable DS is three. With the help of Nuclear Magnetic Resonance (NMR) this DS can directly be measured *de Graaf* et al. [18]. About 0.01 g of the dried acetylated starch was dissolved in 2 cm^3 deuterium-oxide (D_2O).

The NMR apparatus used was a Varian Gemini operating at 200 MHz. To obtain an accurate measurement, the NMR sampled 32 time with a delay between each pulse of 5 s resulting in a better ratio between the signal and the base line. From the obtained spectrum the DS could be obtained. The conversion was measured using gas chromatography (GC). The vinylacetate, acetic acid and acetaldehyde concentrations present in the extruder samples were washed out with methanol. As an internal standard isopropylalcohol (IPA) was added. From this mixture 10×10^{-5} dm^3 was injected in a Hewlett and Packard gas chromatograph (GC). This GC was equipped with a Tenax column.

4 Results and Discussion

4.1 Influence of the screw speed and the screw type on the DS

In Figure 5 the DS as a function of the screw speed and screw type can be found. Both screws differ mainly in length and leakage gaps. The "narrow screws" (L/D = 8 and D =

Tab. 2. DS's and selectivities obtained at varying extruder parameters.

Screw type L = narrow S = wide	Screw speed [RPM]	Vinylacetate [gr/min]	Water [gr/min]	Starch [gr/min]	Alkali molality [mol/gr]	Fully filled length [–]	DS [–]
Temperature	48-70-87-90						
L	15	3.0	6.1	24.5	1.0	4	0.156
L	18	3.0	6.1	24.5	1.0	4	0.150
L	21	3.0	6.1	24.5	1.0	2	0.135
L	23	3.0	6.1	24.5	1.0	2	0.135
L	26	3.0	6.1	24.5	1.0	2	0.115
Temperature	40-75-90						
S	19	3.0	6.1	24.5	1.0	6	0.195
S	23	3.0	6.1	24.5	1.0	6	0.175
S	28	3.0	6.1	24.5	1.0	4	0.200
S	32	3.0	6.1	24.5	1.0	4	0.205
Temperature	48-50-75-90						
L	19	1.0	6.1	24.5	1.0	4	0.068
L	19	1.6	6.1	24.5	1.0	4	0.100
L	19	1.9	6.1	24.5	1.0	4	0.117
L	19	2.3	6.1	24.5	1.0	4	0.145
L	19	2.7	6.1	24.5	1.0	4	0.166
Temperature	50-65-80-90						
L	18.0	1.98	5.74	28	1.0	4	0.144
L	19.8	2.13	6.39	30	1.0	4	0.136
L	23.5	2.53	8.00	36	1.0	4	0.101
L	24.9	2.86	8.62	39	1.0	4	0.120
L	26.5	2.98	9.23	41	1.0	4	0.101
Temperature	40-78-90						
S	19.4	3.0	6.4	24.5	2.0	4	0.147
S	22.4	3.0	6.4	24.5	2.0	4	0.145
S	25.7	3.0	6.4	24.5	2.0	4	0.131
S	28.6	3.0	6.4	24.5	2.0	4	0.143
Temperature	43-58-76-90						
L	19.6	2.7	8.6	24.5	1.0	4	0.160
L	21.6	2.7	8.6	24.5	1.0	4	0.230
L	24.0	2.7	8.6	24.5	1.0	4	0.195
L	26.3	2.7	8.6	24.5	1.0	4	0.245

5 cm) have a flight gap and calander gap of 0.1 mm; the "wide screws" (L/D = 6 and D = 5 cm) have a flight gap and calander gap of 1 mm. All other screw parameters are the same. In the case of the narrow screws the DS decreases as the screw speed increases, the opposite happens in the case of the wide screws. The die resistance was kept the same in all cases. Due to the different geometries the leakage flows differ, resulting in a longer fully filled length for the wide screws compared to the fully filled length of the narrow screws. According to *Speur* et al. [19] and *Ganzeveld* and *Janssen* [11] the shear in the C-shaped chambers is considerably smaller than the shear in a leakage gap. In case of a longer fully filled length the mixing efficiency will increase (Fig. 3) resulting in an earlier starch gelatinisation. Increasing the screw speed in the case of the narrow screws, decreases the fully filled length at a constant die resistance, leading to a lower gelatinisation degree. In this case gelatinisation occurs mainly through heat penetration and not by shear, while for the wide screws, gelatinisation occurs by heat penetration and shear. At the end of the extruder the concentration of vinylacetate appeared, according to GC measurements, to be zero in all cases, all the vinylacetate has reacted. According to *de Graaf* et al. [15] granular starch reacts about 400 times slower compared to gelatinised starch. The longer starch is present in granular form the more vinylacetate will react with alkali. So for the narrow screws the starch granules are gelatinised later at higher screw speed and the longer the gelatinisation process takes, the more vinylacetate has hydrolysed. In the case of the wide screws the length of the partially filled zone stays more or less the

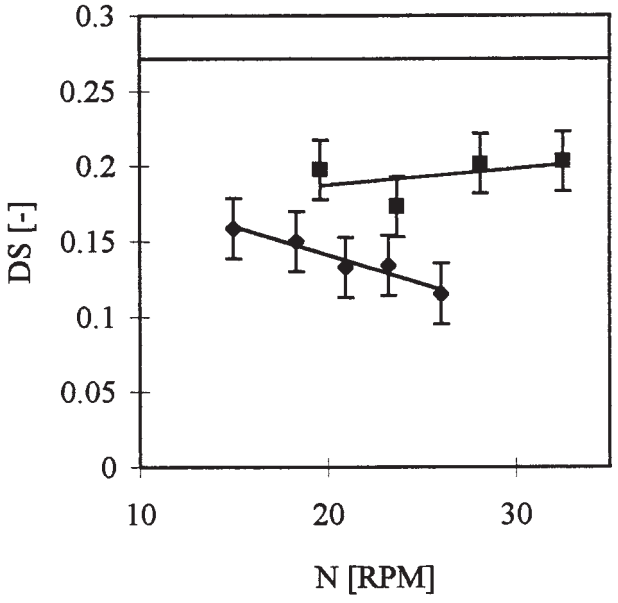


Fig. 5. DS versus screw speed with different extruder screw geometries. ■: L/D 6 wide screws, ◆: L/D = 8 narrow screws, —: Maximum DS.

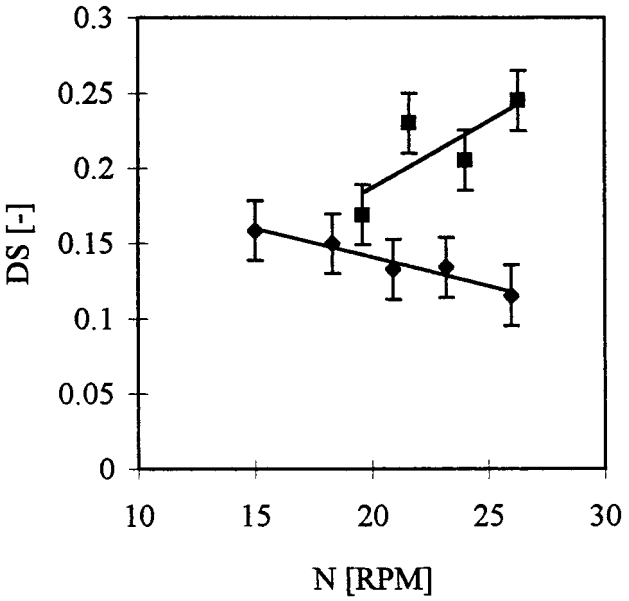


Fig. 6. DS versus screw speed with varying water concentration. (L/D = 8 narrow screws), ♦: 32 wt% water, ■: 37 wt% water.

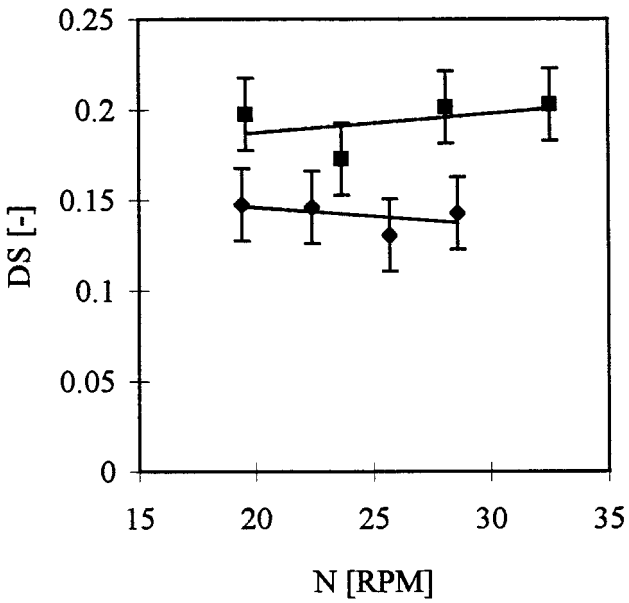


Fig. 7. DS versus screw speed with varying alkali molality. (L/D = 6/wide screws), ■: c_{NaOH} = 1 kmol m^{-3}, ♦: c_{NaOH} = 2 kmol m^{-3}, —: Trend line.

same at increasing screw speed. Starch gelatinisation will stay the same resulting in an almost unaffected DS.

4.2 Influence of the water concentration in the starch gel on the DS

According to Figure 4 a higher starch content means an increased selectivity towards acetylated starch. As has been explained not only the reaction kinetics are important but also the time needed for gelatinisation is important. In the case of an increased water content the gelatinisation time decreases (Fig. 6). So more vinylacetate is able to react with gelatinised starch resulting in a higher DS.

4.3 Influence of alkali molality on the DS

Doubling the alkali molality (Fig. 7) means that the reactions increase by a factor two. So in the first part of the extruder the hydrolysis reaction dominates the acetylation reaction due to the fast that starch is still in its granular form. So even less vinylacetate will be present in a later phase for the acetylation reaction, resulting in lower degree of substitution. It should be reminded that once starch becomes gelatinised, the acetylation reaction dominates both the hydrolysis and the deacetylation reaction and all available vinylacetate will react with the starch.

4.4 Influence of the amount of vinylacetate on the DS

In Figure 8 the influence of the vinylacetate throughput on the DS is shown. Higher vinylacetate throughputs lead to increased DS's. The maximum DS is never reached. During the measurements all other parameters were kept constant. When vinylacetate is supplied at the extruder, only 2.5 g is able to dissolve in 100 g. water. This amount even decreases at higher temperatures (Fig. 9). So only a small part of the vinylacetate will dissolve. Small droplets will be formed from witch vinylacetate will diffuse into the starch gel. As a result increasing of the feed of vinylacetate will not lead to a higher vinylacetate concentration in the starch gel. This statement was verified by splitting the feed of vinylacetate. One part was supplied in the beginning of the extruder, while the other part was supplied in a later part of the extruder (zone 3, Fig. 1). The DS obtained in this way was exactly the same as the DS obtained when all the vinylacetate was added

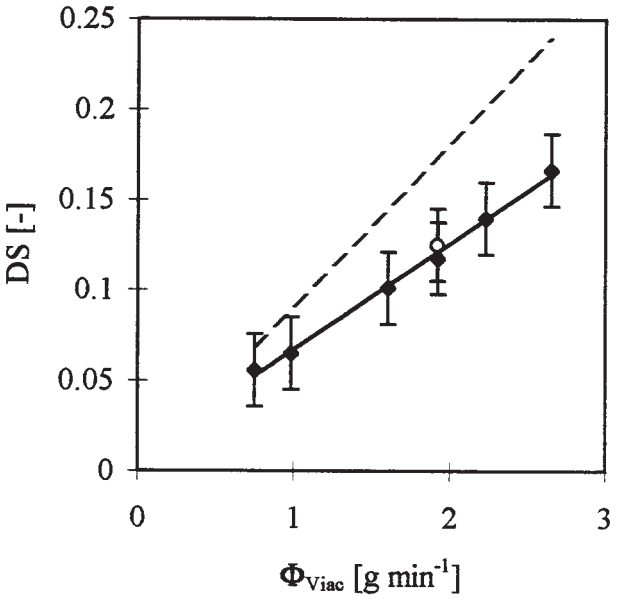


Fig. 8. DS versus vinylacetate throughput. (L/D = 6/wide screws), ♦: Vinylacetate throughput in zone 1 of the extruder, ○: Vinylacetate throughput in zone 3 of the extruder, —: Trend line, – –: Maximum DS.

in the beginning of the extruder. It also proves that starch has not gelatinised before zone 3. If starch would have been gelatinised in that part a higher DS should have been obtained.

4.5 Varying the screw speed at a constant relative throughput

Increasing the screw speed at a constant relative throughput (α_{rel}) in the case of the narrow screws, shows that the DS decreases (Fig. 10).

$$\alpha_{rel} = \frac{Q_r}{Q_{th}} \qquad [13]$$

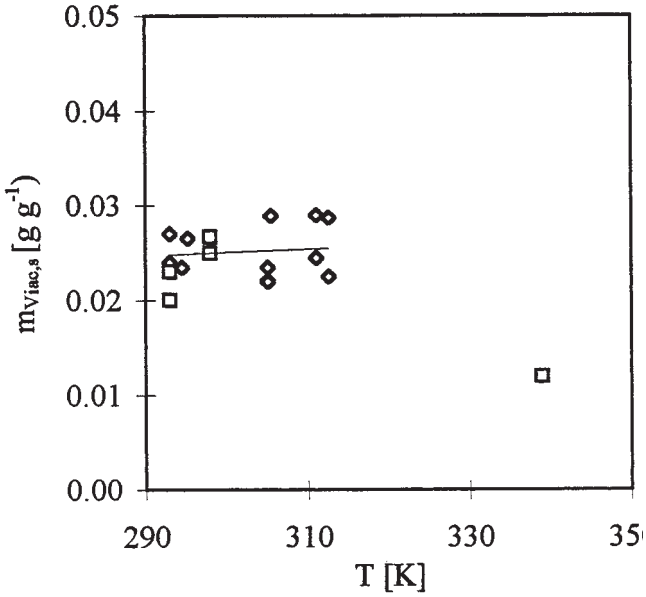


Fig. 9. Solubility of vinylacetate in water at different temperatures [20]. ◇ Measurements, □ Literature [6], — Fit.

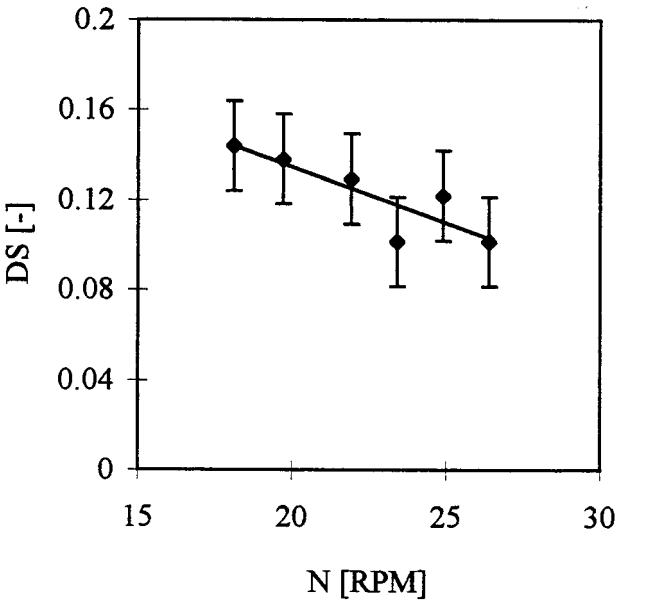


Fig. 10. DS versus screw speed at a constant relative throughput. (L/D = 8/narrow screws), ◆: Measurements, —: Trend line.

Q_r is the real throughput and Q_{th} is the theoretical throughput. At increasing screw speed Q_{th} increases which will result in a changing leakage flow in the case that the screw speed is varied. Keeping α_{rel} constant results in constant relative leakage flows. So it should be expected that a constant DS should be obtained at a constant relative throughput, but as has already been stated, the fully filled length of the extruder with a small leakage gap is nearly independent of these variables. Because of the decrease in residence time a negative dependency at an increasing screw speed results.

4.6 The reactive extrusion interaction diagram

By incorporating the reaction parameters of the acetylation of starch in an interaction diagram of the counter rotating twin screw extruder a reaction extrusion interaction diagram is achieved. The aim of this diagram is to analyse the machine performance and to elicit the general tendencies of the reactor performance in the extruder. In Figure 11 this diagram is presented. In the diagram, the primary variables of the extruder are the screw speed, the throughput, the temperature, the die-resistance and the screw geometry. For the reaction the water percentage and the reactant throughputs are the primary variables. All other variables can only be influenced indirectly by changing the primary variables. Residence time, shear, alkali molality and the water percentage are the most important variable that have influence on the gelatinisation behaviour of starch. The sooner gelatinisation occurs at high temperatures and starch concentrations, the higher the DS and selectivity will be. It can be seen that the gelatinisation rate is function of the waterpercentage and thus the starch concentration. The higher the water percentage the sooner starch gelatinises while on the other hand the selectivity drops. Temperature has in all cases a positive effect, the gelatinisation and the reaction rate increases.

5 Conclusions

- Because of the competing character of the acetylation reaction of gelatinised starch and the hydrolyis reaction of the vinylacetate an early gelatinisation in the extrusion process is important for a high selectivity of the process. This gelatinisation can be positively influenced by increasing the leakage gaps, the temperature, the alkali concentration and the water concentration.
- Increasing the vinylacetate concentration results in a proportional increase of the DS.
- Increasing the screw speed for screws with large leakage gaps (> 1 mm) has a positive influence on the gelatinisation of starch and thus a higher DS is obtained. The opposite will happen for screws with small leakage gaps (< 0.1 mm).

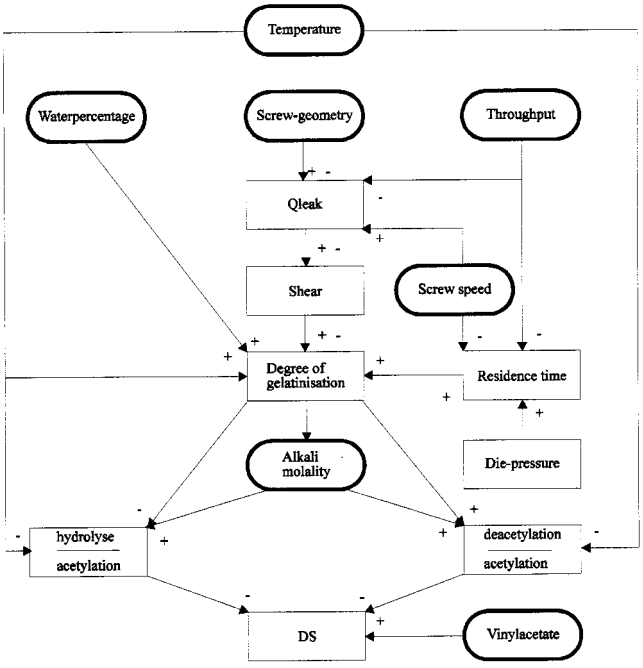


Fig. 11. Steady state interaction diagram for starch modification reactions.

6 Nomenclature

A:	Constant dependant on the screw geometry	(m^3)
B:	Constant dependant on the screw geometry	(m^3)
c:	Concentration	(mol m^{-3})
DS:	Degree of substitution	(–)
E_a:	Activation energy	(J mol^{-1})
E_{eff}:	Mixing efficiency	(–)
k:	Reaction constant	(m^3 mol^{-1} s^{-1})
$k_\circ$:	Frequency factor	(m^3 mol^{-1} s^{-1})
K:	Reciprocal die resistance	(m^3)
K_{eq}:	Dissociation constant of starch	(–)
K_a:	Dissociation constant of water	(–)
m:	Amount of threat starts	(–)
M:	Molar mass	(g mol^{-1})
N:	Screw speed	(RPM)
K_S:	Dissociation constant of starch in an alkaline surrounding	(–)
ΔP_c:	Pressure difference in a C-shaped chamber	(Pa)
pK_{eq}:	–Log (K_{eq})	(–)
pK_S:	–Log (K_S)	(–)
Q_{th}:	Theoretical throughput	(m^3 min^{-1})
Q_r:	Real throughput	(m^3 min^{-1})
Q_{leak}:	Total leakage throughput	(m^3 min^{-1})
Q_t:	Leakage throughput in the tethraeder gap	(m^3 min^{-1})
Q_f:	Leakage throughput in the flight gap	(m^3 min^{-1})
Q_c:	Leakage throughput in the calander gap	(m^3 min^{-1})
Q_S:	Leakage throughput in the side gap	(m^3 min^{-1})
R:	Gas constant	(J mol^{-1} K^{-1})
T:	Temperature	(K)
t:	Time	(s)
V_c:	Volume of a C-shaped chamber	(m^3)
Φ_v:	Volumetric feed rate	(m^3 s^{-1})
η_c:	Viscosity in a C-shaped chamber	(Pa s)
σ_{AS}:	Selectivity towards acetylated starch	(–)
ROH:	Starch hydroxyl group	
RO^-:	Dissociated starch hydroxyl group	
NaOH:	Sodium hydroxide	
Viac:	Vinylacetate	
RAc:	Acetylated starch	
pf:	Partially filled zone	
ff:	Fully filled zone	

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